Controlled chemical polymerization of conducting polymers

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Abstract

Electronically conducting polymers are a special category of organic macromolecules that have the special property of becoming electrically conductive under appropriate conditions. Since their discovery thirty years ago, there has been interest in applying these materials in many areas, including molecular electronics, anti-corrosive coatings, and electromagnetic shielding. However, very few technologies have emerged from beyond the laboratory proof-of-concept stage, largely due to the difficulty in processing these polymers into useful forms. This paper describes the method of controlled growth polymerization to produce conducting polymers using conventional processing methods such as spin coating, and without restriction on the chemical nature of the polymer.

Résumé

Les polymères conducteurs électroniques constituent une catégorie spéciale de macromolécules organiques qui possèdent la propriété particulière de devenir électro-conductrices dans des conditions appropriées. Depuis qu'ils ont été découverts, il y a une trentaine d'années de cela, on a cherché à appliquer ces matériaux dans de nombreux domaines, entre autres en électronique moléculaire, comme revêtements anti-corrosion et comme matériaux de protection électromagnétique. Toutefois, ces polymères n'ont guère donné lieu à l'émergence de nouvelles technologies au delà de la validation de principe en laboratoire, principalement en raison de la difficulté que comporte leur transformation en formes utiles. Dans cet article, on décrit la méthode de polymérisation à croissance contrôlée utilisée pour produire des polymères conducteurs à l'aide de méthodes classiques, telles que l'application par centrifugation, sans restriction sur la nature chimique du polymère.

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Executive summary

Controlled Chemical Polymerization of Conducting Polymers

Colin G. Cameron, Michael S. Freund; DRDC Atlantic SL 2005-192; Defence R&D Canada – Atlantic; December 2005. Published in: Proceedings of the 11th CF/DRDC Meeting on Naval Applications of Materials Technology.

Background

Electronically conducting polymers are a special category of organic macromolecules that have the special property of becoming electrically conductive under appropriate conditions. Since their discovery thirty years ago, there has been interest in applying these materials in many areas, including molecular electronics, anti-corrosive coatings, and electromagnetic shielding. However, very few technologies have emerged from beyond the laboratory proof-of-concept stage, largely due to the difficulty in processing these polymers into useful forms.

Principal Results

The work presented in this paper illustrates an alternate approach to growing conducting polymers. Traditional methods generally yield polymer as an insoluble, unworkable solid. The technique demonstrated here exploits the delicate thermodynamic balance that can be reached when the oxidant is chosen carefully to have a formal potential less positive than the monomer. This leads to a metastable solution that can be processed by various techniques, such as spraying or spin-coating. When the solvent has evaporated leaving some critical concentration of reagents, the reaction accelerates, leaving a high-quality polymer film.

Significance of Results

The demonstration of a general route to the production of processible conducting polymers is a major step forward in this field. This methodology presents many new opportunities for conducting polymer applications

Future Work

In the short term, we intend to adapt these processing methods for use in our ongoing interest in dielectric composites. Other directions for future investigations include the formation of porous conducting polymer electrodes for energy storage applications, and multilayered

conducting polymer apparatus for all-organic electrochromic devices for applications such as active camouflage.

Sommaire

Controlled Chemical Polymerization of Conducting Polymers

Colin G. Cameron, Michael S. Freund; DRDC Atlantic SL 2005-192; R & D pour la défense Canada – Atlantique; décembre 2005. Publié dans: Proceedings of the 11th CF/DRDC Meeting on Naval Applications of Materials Technology.

Introduction

Les polymères conducteurs électroniques constituent une catégorie spéciale de macromolécules organiques qui possèdent la propriété particulière de devenir électro-conductrices dans des conditions appropriées. Depuis qu'ils ont été découverts, il y a une trentaine d'années de cela, on a cherché à appliquer ces matériaux dans de nombreux domaines, entre autres en électronique moléculaire, comme revêtements anti-corrosion et comme matériaux de protection électromagnétique. Toutefois, ces polymères n'ont guère donné lieu à l'émergence de nouvelles technologies au delà de la validation de principe en laboratoire, principalement en raison de la difficulté que comporte leur transformation en formes utiles.

Résultats principaux

Les travaux présentés dans cet article décrivent une autre méthode permettant d'obtenir des polymères conducteurs. En général, les méthodes classiques donnent un polymère solide et insoluble qui ne peut être façonné. La technique décrite dans cet article exploite le délicat équilibre thermodynamique qui peut être atteint lorsqu'on sélectionne soigneusement l'oxydant pour que son potentiel formel soit moins positif que celui du monomère. On obtient alors une solution métastable qui peut être traitée par diverses techniques, telles que la pulvérisation et le revêtement par centrifugation. Une fois le solvant chassé par évaporation, ce qui laisse une certaine concentration critique de réactifs, la réaction s'accélère et donne une pellicule de polymère de haute qualité.

Portée

La démonstration d'un procédé général permettant de produire des polymères conducteurs pouvant être transformés constitue une importante avancée dans ce domaine. Cette méthodologie ouvre de nombreuses portes vers des applications comportant des polymères conducteurs.

Recherches futures

Nous tenterons, à court terme, d'adapter ces méthodes à nos projets actuellement en cours sur les composites diélectriques. Parmi les autres orientations que pourront prendre les recherches futures, on compte la formation d'électrodes poreuses en polymères conducteurs destinées à être utilisées pour le stockage d'énergie, et les appareils à polymères conducteurs multicouches pour dispositifs électrochromes entièrement organiques destinés à être utilisés dans des applications comme le camouflage actif.

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1 Background

Electronically conducting polymers are a special category of organic macromolecules that have the special property of becoming electrically conductive under appropriate conditions. The common feature of these materials is the infinite conjugated backbone, as illustrated in Figure 1 with three common polymers.

Not surprisingly, there has been a lot of interest in these materials since their discovery in the mid-1970s. Molecular electronics, anti-corrosive coatings, and electromagnetic shielding are among the proposed applications for conducting polymers. However, very few technologies have emerged from beyond the laboratory proof-of-concept stage, largely due to the difficulty in processing these polymers into useful forms. Synthesis is usually straightforward and can often be achieved chemically using an oxidation radical-coupling mechanism. This is an important feature that will be discussed later in this paper.

The extended delocalized π-bond network present in conducting polymers leads to a band-like electronic structure. Conductivity is attained when mobile charge carriers are present in the valence (highest occupied) or the conducting (lowest unoccupied) band. For all known conducting polymers, the energy gap between these bands is sufficiently large that it cannot be overcome by thermal energy alone.[1] Instead, it is necessary to generate these charge carriers through some other means, most frequently by oxidizing the polymer and thus leaving mobile positive charges or "holes" in the band structure. This condition is similar to that found in semiconductor science, and shares the common name "doping."

The charge carriers, or "polarons" organize into pairs ("bipolarons") a few bonds apart. Despite the electrostatic repulsion, this arrangement is energetically favoured due to spin pairing. It can be intuitive (although perhaps not rigorously accurate) to think of charge transport arising from the motion of these bipolarons along the polymer backbone through the rearrangement of bonds. This is illustrated in Figure 2. The rearrangement of single and double bonds presents only a small energy barrier to the movement of the total unit. Consequently, the process is rapid, leading to the high conductivity characteristic of conducting polymers. This can be as high as 10^2 S/cm, which is comparable to the conductivity of graphite.

The most popular and convenient method of growing this kind of polymer is through an oxidation and radical coupling approach, shown in Figure 3. There are two key steps, the importance of which will be apparent later. The first step is the oxidation— chemical or electrochemical— of the monomer unit, pyrrole in this case. In the second step, the monomer radical cations couple to form dimers. The dimers are then oxidized and react with radical cation monomers or other radical cation dimers, and so on.

[1] A hypothetical small bandgap polymer could have a significant quantity of electrons leave the valence band and enter the conduction band, in accordance with Boltzmann distribution. With the spontaneous generation of such charge carriers, the material would be described as an *inherently* conducting polymer.

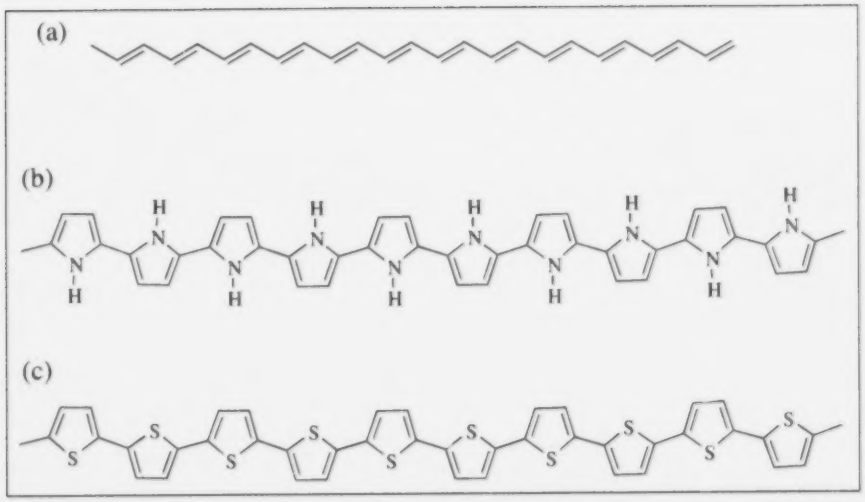


Figure 1: *Three conducting polymers:(a) Polyacetylene, (b) Polypyrrole, and (c) Polythiophene.*

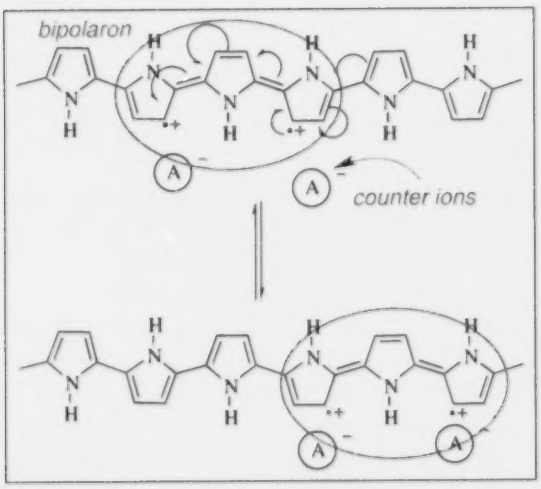


Figure 2: *Motion of a bipolaron charge carrier through bond rearrangement.*

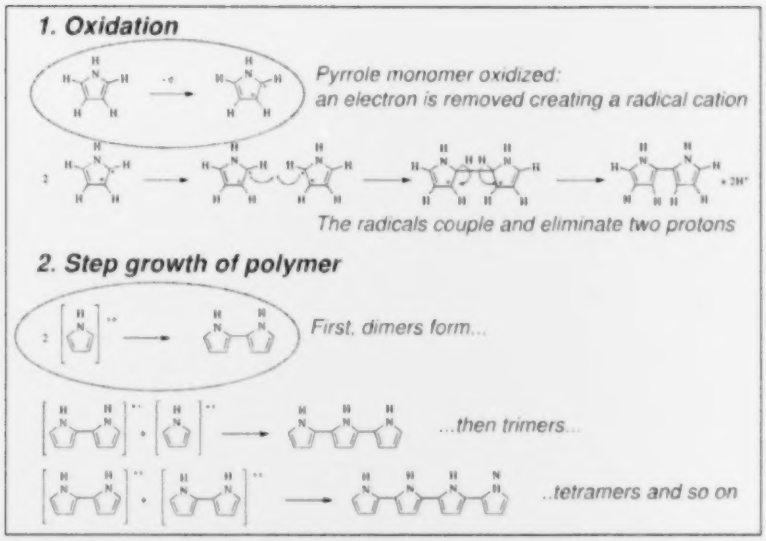

1. Oxidation
Pyrrole monomer oxidized:
an electron is removed creating a radical cation
The radicals couple and eliminate two protons
2. Step growth of polymer
First, dimers form...
...then trimers...
..tetramers and so on

Figure 3: *Mechanism for pyrrole polymerization*

Polymer can be produced in this way quite easily. Electrochemically, polymer can be grown on the surface of an electrode. Larger scale production can be done by mixing solutions of the polymer and an appropriate chemical oxidant. Yet despite this simple chemistry, the industrial applications of these polymers have been few. This is largely due to the difficulty in processing the polymers; typically, chemical growth rapidly produces polymer as a black precipitate that is resistant to solvents and to melting, despite being nominally a thermoplastic. The extended π systems of the polymers result in strong attractive forces between neighbouring chains, a phenomenon known as π stacking.

Attempts to improve the solubility of conducting polymers are not new. One reasonably successful approach is to attach pendant groups to the backbone, giving a "handle" to which solvent can attach to pull the main chain into solution. Furthermore, large bulky groups such as the alkyl substituents shown in the example in Figure 4 can push other chains away. There are at least three main problems to this approach. First, the side-groups add a new layer of complexity to the monomer synthesis, and in some cases be non-trivial. Second, the presence of the sidechains changes the electronic structure of the monomer and consequently the polymer. This is not always undesirable, but it can be a limitation. Third, the bulky pendant groups exert twisting forces on the rings, leading to reduced coplanarity. The torsion in turn leads to reduced p-orbital overlap, which translates to diminished *pi*-conjugation, a greater band gap, and lowered conductivity. An illustration of this phenomenon is in Figure 5. This quantum chemical calculation uses Density Function Theory (DFT) calculations at the B3LYP/6-31G(d)//B3LYP/3-21G(d) level of theory with a polarizable continuum model for the solvent (acetonitrile). For bipyrrole, the most stable geometry occurs when the rings are nearly coplanar, with a torsion of 6°. When rel-

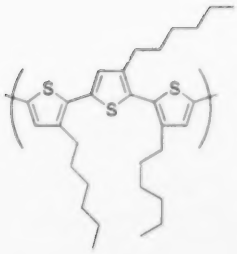
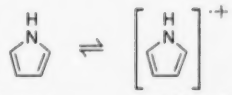


Figure 4: *Using substituents to improve solubility: poly(3-hexylthiophene)*

atively small butyl groups are added, the optimized geometry shows a ring torsion of 51°. Furthermore, the energy gap between the highest occupied and lowest unoccupied orbitals increases by 0.49 eV in the substituted bipyrrole, a significant amount.

2 Cascade Polymerization

In order to avoid the problems of rapid precipitation of intractable polymer, a controlled growth method is called for. As mentioned previously, there are two key steps in the polymerization process. First is the generation of the oxidized species, Equation 1. Note that this is a thermodynamic equilibrium as governed by the Nernst Equation (Equation 2).



Reduced *Oxidized* (1)

$$E = E^0 + \frac{RT}{nF} \log \frac{[Ox]}{[Red]} \tag{2}$$

The concentration ratio of the oxidized species to the neutral monomer at some potential E is a function of E^0 (the formal potential, which is a thermodynamic characteristic of any electrochemically active species), the constants R and F (the gas constant and Faraday's constant, respectively), the temperature T, and the number n of electrons involved. This indicates that a using an oxidant with a potential *less positive* that of the pyrrole will maintain the equilibrium so that the unreactive reduced form dominates. Note that in general E^0 becomes lower in magnitude as the number of attached monomers increases. For pyrrole, $E^0_{\text{pyrrole}} > E^0_{\text{bipyrrole}} > E^0_{\text{terpyrrole}}$ and so on; bipyrrole is more easily oxidized than pyrrole.

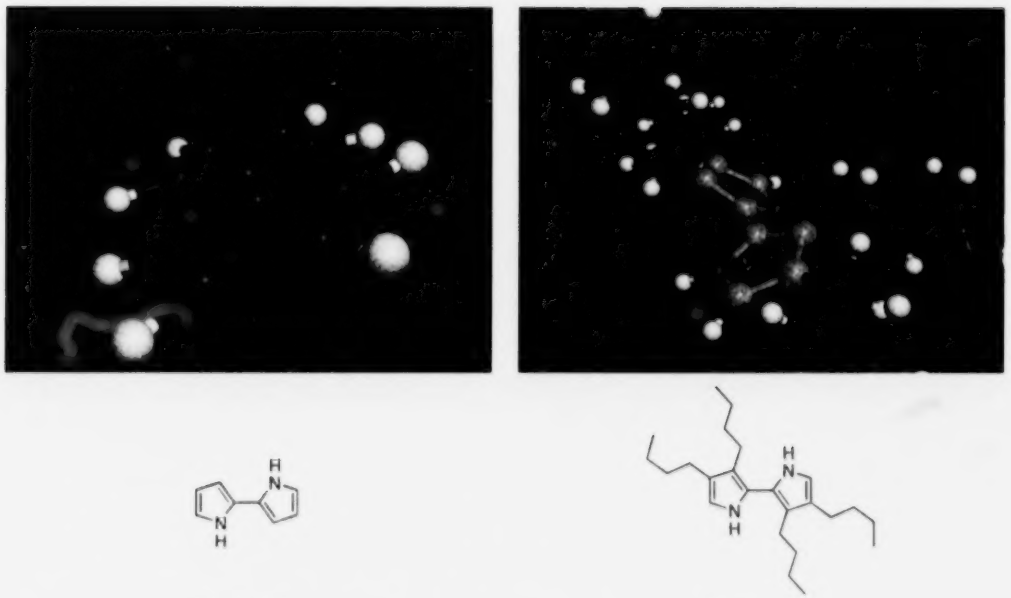
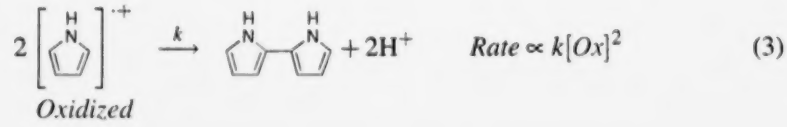


Figure 5: *Dihedral ring angle in bipyrrole (left) and butyl-substituted bipyrrole (right). In the latter, the rings are more lightly coloured for emphasis.*

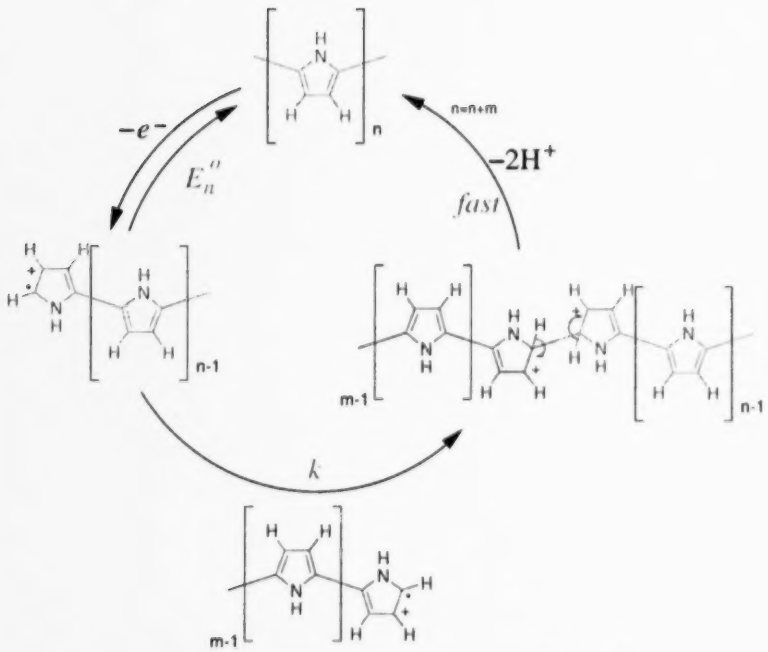
The second consideration is one of kinetics. The dimerization (and similar reactions with larger species) reaction should follow simple second-order kinetics, Equation 3.



This implies that polymerization will not occur at any appreciable rate until the concentration of radical cation builds. Conventionally, this is not an issue, since sufficient monomer is present in solution to generate polymer, and all the monomer is immediately converted to the radical cation when a strong oxidant is used. When a weak oxidant is employed, only a small fraction of the monomer will be in the radical cation state. Furthermore, if the solution is dilute, reaction Equation 3 will essentially not proceed.

The key to controlled growth polymerization is concentration manipulation. The ratio of reduced to oxidized monomer will always be constant as dictated by the Nernst Equation. If the solution containing monomer and oxidant is allowed to evaporate slowly, then the absolute concentration of oxidized monomer will grow, eventually reaching a point where reaction Equation 3 can proceed rapidly. Until this concentration is reached, the solution of monomer and oxidant can be considered metastable. It can be processed in the same way as any dilute polymer, such as by spraying or spin coating. When the solution has evaporated sufficiently, conducting polymer will be produced in the as-processed state.

Figure 6 illustrates the cascade growth mechanism cycle. Initially, $n = m = 1$ and the concentration of the monomer is low. Due to the relative values of the formal potentials of the monomer and oxidant, the unreacted monomer (top of the cycle) dominates. Slowly, as solvent evaporates, some small quantity of oxidized monomer will be able to react, completing the low part of the circle with rate k. This will form dimer, $n = 2$. Since the dimer is more easily oxidized, *i.e.*, $E_1^0 > E_2^0$, it will tend to exist to a greater degree in its oxidized state; the bottom part of the cycle occurs more rapidly. The cycle continues to accelerate in this manner, leading to rapid formation of the polymer. To reiterate: going from a metastable solution of reagents to a final polymer involves the key step of surpassing some critical concentration where the bottom half of the cycle can proceed at an appreciable rate. This can be done easily by allowing the solvent to evaporate slowly. When the film has formed, excess monomer and oxidant can be rinsed away.



$$Rate \propto k[n-mer][m-mer] \qquad E_n^0 > E_{(n+1)}^0$$

Figure 6: *Cascade growth polymerization cycle.*

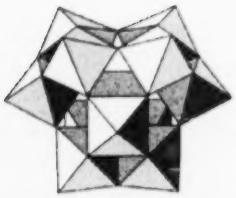


Figure 7: *The α-Keggin structure shown as an assemblage of 12 [MO_6] octahedra and a [XO_4] tetrahedron and having an overall diameter of 14 Å.*

3 Results

3.1 Choice of oxidant

Phosphomolybdic acid (PMA), $H_3PMo_{12}O_{40} \cdot xH_2O$, is one of many polyoxometallates that have been of interest due to their catalytic and electrochemical properties [1]. Its formal potential $E^0 \approx 0.4$ V is significantly lower than pyrrole's $E^0 \approx 1.0$ V, implying that an equilibrium of around 1 in 10^{10} pyrrole molecules in the oxidized state (see Equation 2). The oxidant exhibits a distinct rhombohedral geometry, the α-Keggin structure illustrated in Figure 7. This gives rise to a distinct X-ray diffraction (XRD) spectrum peak at $2\theta = 8.95°$ that disappears after the PMA has reacted (Figure 8).

This characteristic XRD feature leads to some interesting ramifications in the synthesized polymer. Figure 9 shows the spectra of polypyrrole prepared using either the new PMA method or the more conventional strong oxidant ($FeCl_3$) approach. The diffraction pattern of the latter shows a broad halo in the $2\theta = 15°$ to $35°$ region, corresponding to the randomly ordered structures in the polymer. The pattern of the polypyrrole grown using PMA and subsequently rinsed with tetrahydrofuran (THF) also has this halo along with a clear diffraction peak around $2\theta = 8°$ which must somehow be associated with the polyoxometallate. There are two possibilities: first, some PMA has remained in the film. Second, the PMA was successfully removed with rinsing, but left behind a templated structure. Rinsing with strong acid (H_2SO_4) in addition to THF did not eliminate the peak, supporting the second possibility. Furthermore, there was no evidence of PMA in the cyclic voltammetry of the films.

Further evidence of the complete removal of the PMA is found in the infrared spectra of the polymers. Fourier transform infrared (FTIR) spectroscopy of polypyrrole grown with PMA is very similar to a film grown using $FeCl_3$ as the oxidant (Figure 10) and completely dissimilar to the spectrum of PMA alone, indicating the absence of PMA in the sample.

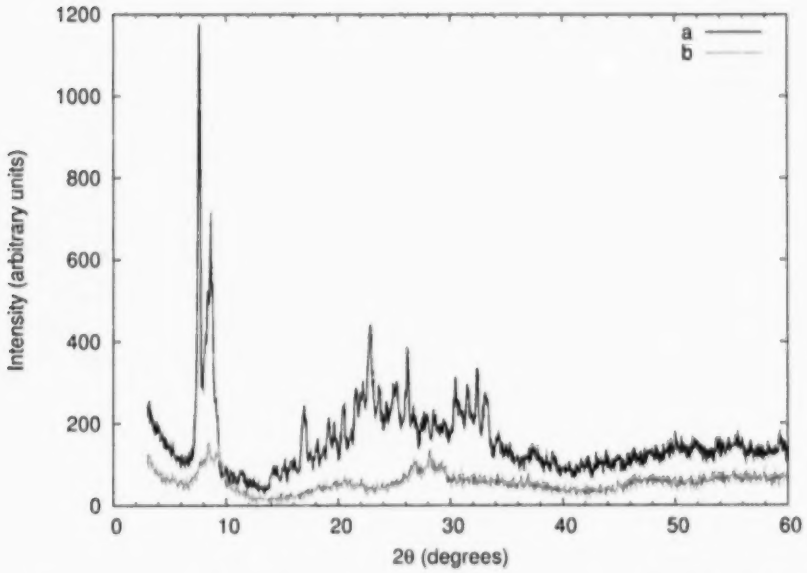


Figure 8: *X-ray pattern of (a) Phosphomolybdic acid cast from THF, and (b) Phosphomolybdic acid in its reduced form.*

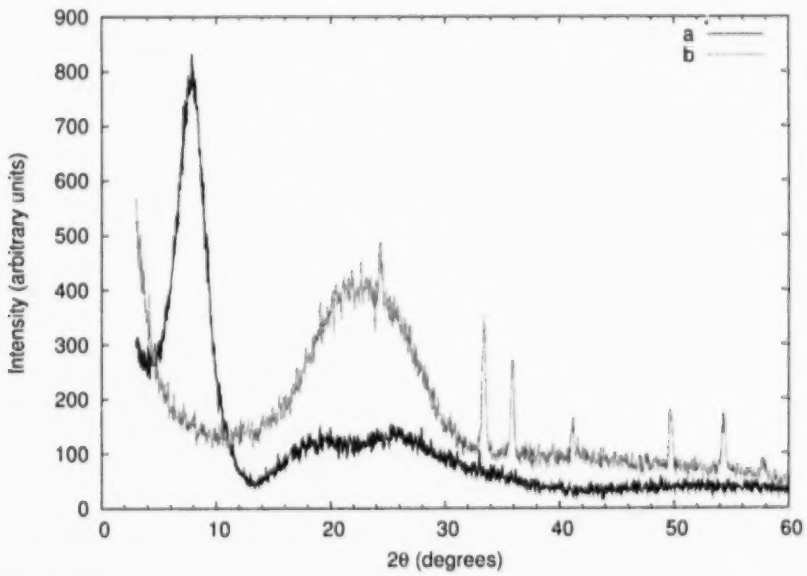


Figure 9: *X-ray diffraction pattern of polypyrrole chemically synthesized with either (a) phosphomolybdic acid or (b) $FeCl_3$.*

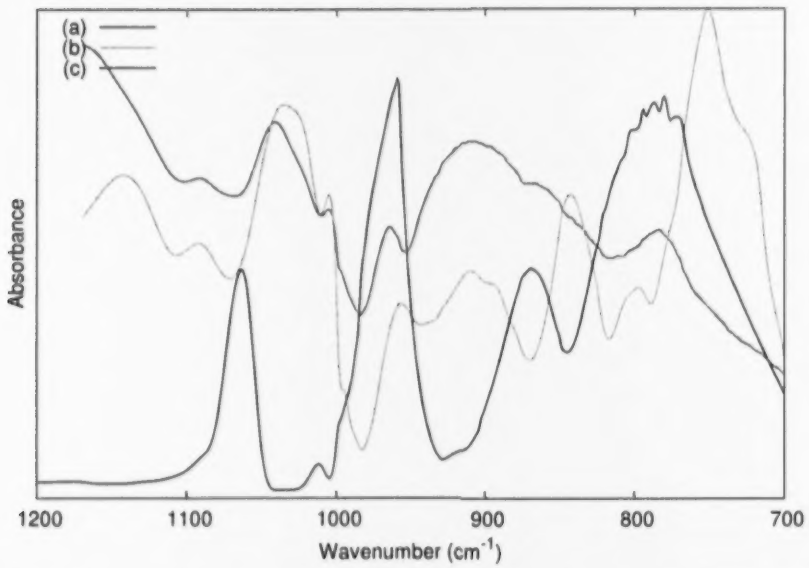


Figure 10: *FTIR spectra of (a) polypyrrole prepared with $FeCl_3$, (b) polypyrrole film formed with phosphomolybdic acid and rinsed with H_2SO_4, and (c) phosphomolybdic acid.*

3.2 Composite materials

3.2.1 Interpenetrating polymer networks

The addition of conducting polymers to existing structurally robust polymers as interpenetrating polymer networks opens up the possibility of a number of exciting new hybrid materials. The proposed sequence was straightforward: (i) swell the polymer with an appropriate solvent, (ii) introduce the reagents for controlled growth polymerization, (iii) rinse away excess reagents and reacted PMA. This concept was illustrated using a latex rubber glove. An IPN could successfully grown by first swelling and impregnating the latex with a solution of oxidant in THF , and then exposing the film to an atmosphere saturated in THF and containing pyrrole vapour. After allowing the polymerization to continue overnight, the excess materials were rinsed away. The film was dried and rinsed with ethanol (which does not cause swelling).

The resulting films were examined by Scanning Electron Microscopy (SEM) . There were no apparent clusters of polymer or reagents on the surface; these were seen in other experimental methods that were deemed unsuccessful. Figure 11 shows such a surface, and Figure 12 shows the cross section of a freeze-fractured IPN membrane. An interesting feature of these materials is that they do not require the usual conductive coating needed for SEM. This is an indication that the interpenetrating polypyrrole fibres are sufficiently abundant and well-distributed that the whole matrix is sufficiently conductive to dissipate

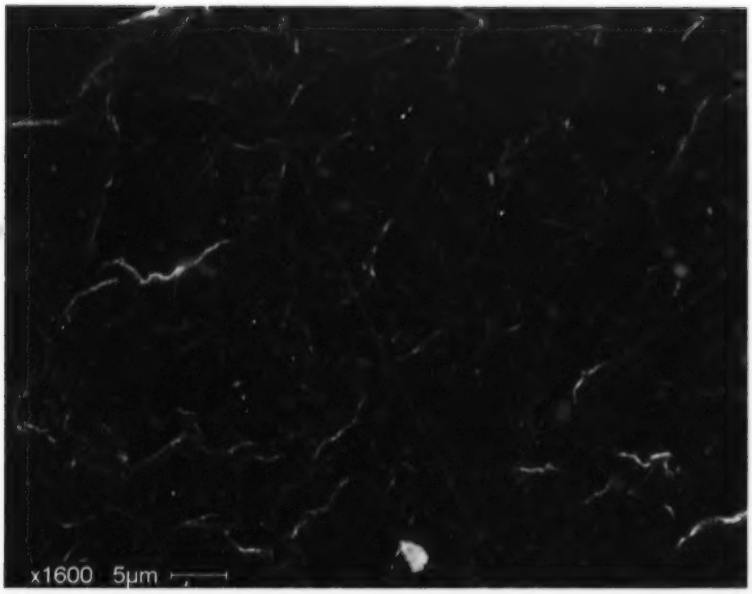


Figure 11: *SEM image of the surface of a polypyrrole-latex IPN.*

the charge of the electron beam. If this charge were not dissipated, the images would be expected to be white and blurry. Even the freeze-fracture cross section images indicate good distribution of the guest polypyrrole.

3.2.2 Coprecipitated thermoplastics

As an extension to the work with latex, the controlled growth polymerization method was applied where the "host" polymer was soluble. This approach lends itself to better control of the composition of the final materials and also perhaps to larger-scale synthesis. Pellethane 2103-70A (Dow), a thermoplastic polyurethane with which our laboratory has previous experience, was selected. In essence, the synthetic procedure consisted of mixing solutions of Pellethane and monomer with solutions of the oxidant, and processing the resulting mixture in accordance with the steps described earlier.

Spin-coated films of 1:1 Pellethane:polypyrrole composites showed remarkably flat and regular surface morphology, with no evidence of phase separation on the scale of SEM (Figure 13) or atomic force microscopy (AFM) (Figure 14). The quality of these films indicates that this is a good route to producing quality, homogeneous composites of conducting polymers and a support matrix. This is a noteworthy development, since this will permit the development of materials having the desirable electronic properties of conducting polymers with the environmental and physical stability of commercial thermoplastics.

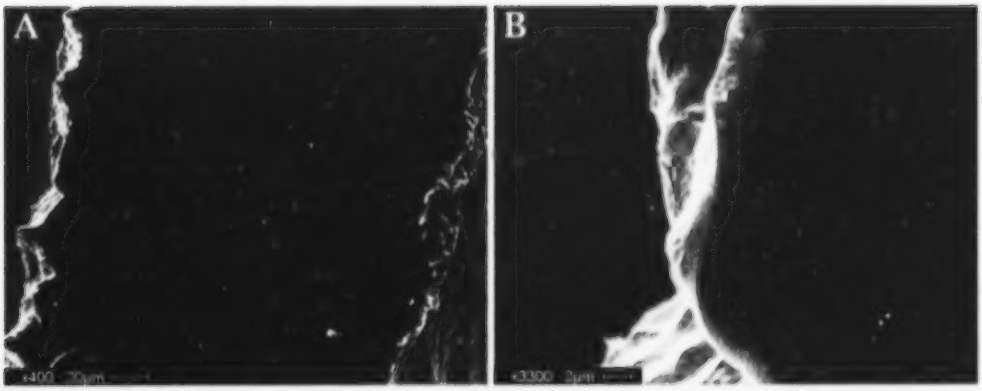


Figure 12: *SEM image of the cross section of a polypyrrole-latex IPN.*

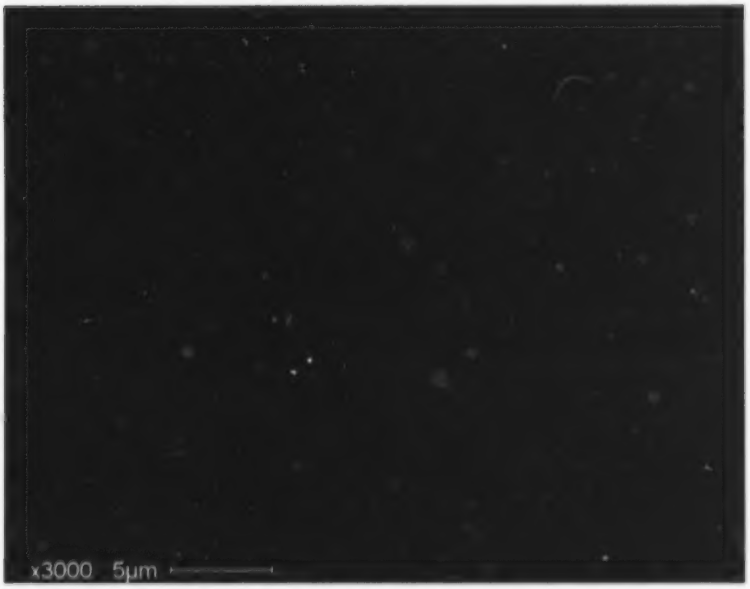


Figure 13: *SEM image of a spin-coated film of 1:1 Pellethane:polypyrrole composite.*

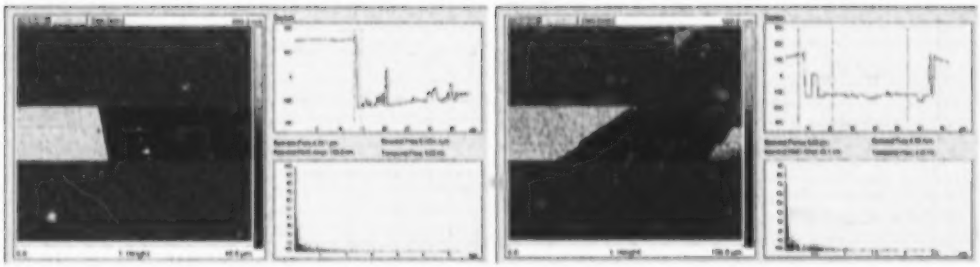


Figure 14: *AFM images of spin-coated (a) polypyrrole, and (b) 1:1 Pellethane:polypyrrole composite.*

Some preliminary work was done to examine the effect of polypyrrole loading on the conductivity of the Pellethane composites. This ties in with our ongoing interest in the dielectric properties of filled materials [2, 3, 4, 5, 6]. The conductivity profile (Figure 15) follows a sigmoidal shape as would be expected for a percolative system. For the Pellethane/polypyrrole composites, the percolation threshold occurs at around 8% w/w loading. This is significantly lower than Pellethane/graphite systems, where the percolation threshold was around 18%.

3.2.3 Extension to other polymer systems

The bulk of this work was done with the PMA and polypyrrole combination. To illustrate the broad applicability of this process, a second combination was chosen. Polythiophene is another popular conducting polymer, and so it is a logical choice. The formal potential of the thiophene monomer $E^0_{\text{thiophene}} = 1.9$ V is considerably more positive than pyrrole, $E^0_{\text{pyrrole}} = 1.0$ V. It should be possible to induce controlled growth polymerization if an oxidant with a correspondingly higher formal potential was chosen ($E^0_{\text{PMA}} \approx 0.4$ V), however in order to minimize the number of variable being changed, it was decided that bithiophene ($E^0_{\text{bithiophene}} = 1.05$ V and PMA would be a suitable combination.

Cyclic voltammetry of polythiophene films grown from bithiophene monomer using either electrochemical growth or controlled chemical growth are presented in Figure 16. The shapes of the voltammograms are similar, reflecting the similarity in the products of both methods. The broader current envelope of the chemically grown polymer suggests that it may be of a higher quality than the electrochemically grown film. There is also no indication of PMA being left in the film.

And even better agreement is evident in the FTIR spectra of the polymers (Figure 17), and again there is no evidence of PMA being present.

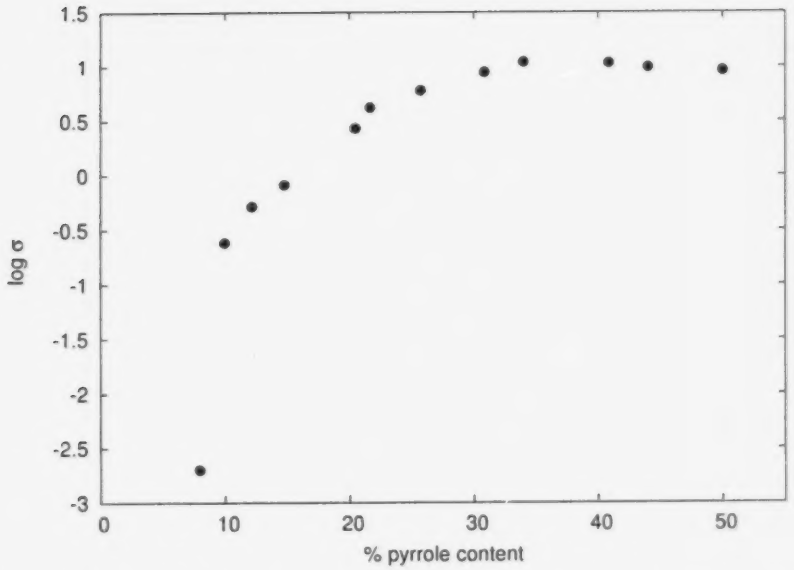


Figure 15: *Conductivity–loading relationship for Pellethane/polypyrrole composites*

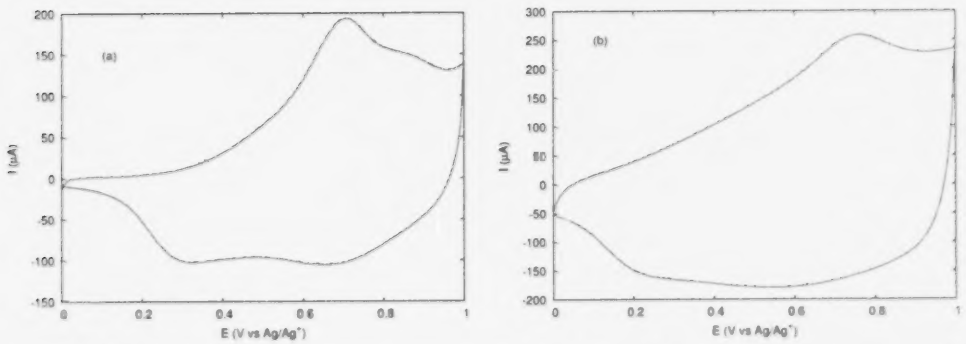


Figure 16: *Cyclic voltammograms of polythiophene grown (a) electrochemically, and (b) using controlled growth polymerization.*

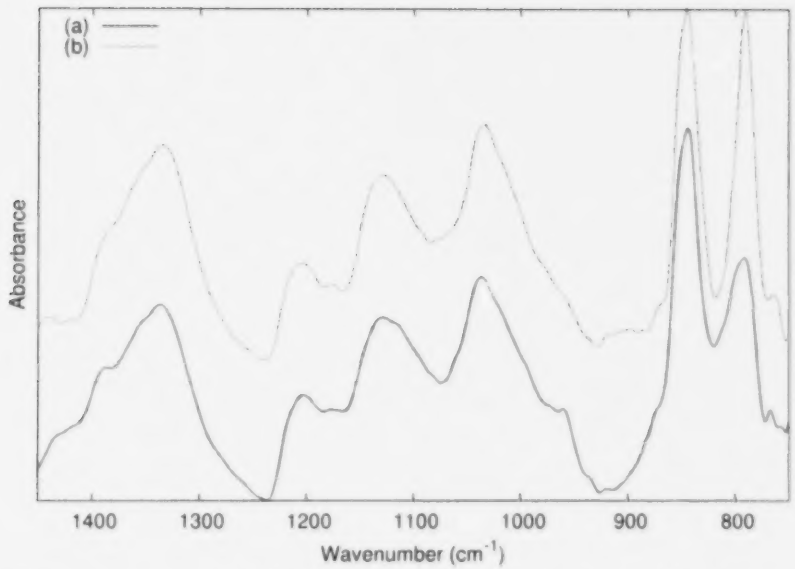


Figure 17: *FTIR spectra of polythiophene grown (a) with PMA, and (b) electrochemically.*

4 Conclusion

This work as clearly demonstrated controlled growth polymerization as a viable means of producing high quality films of polypyrrole and polythiophene. The key consideration is the judicious choice of monomer and oxidant based on the formal potentials E^0 of both. Under dilute conditions, a metastable solution results, and this solution may be processed through spin coating or any other means. The processing can include other polymers, either to form interpenetrating conducting polymer networks within a support host, or can be a coprecipitation to yield high quality composites. This in turn suggests the possibility of a variety of new materials with useful properties. Finally, this methodology should be broadly applicable to a range of different monomers with specific electronic properties. This implies the possibility of engineering all-organic electronic devices such as organic LEDs and molecular circuitry using this approach.

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Electronically conducting polymers are a special category of organic macromolecules that have the special property of becoming electrically conductive under appropriate conditions. Since their discovery thirty years ago, there has been interest in applying these materials in many areas, including molecular electronics, anti-corrosive coatings, and electromagnetic shielding. However, very few technologies have emerged from beyond the laboratory proof-of-concept stage, largely due to the difficulty in processing these polymers into useful forms. This paper describes the method of controlled growth polymerization to produce conducting polymers using conventional processing methods such as spin coating, and without restriction on the chemical nature of the polymer.

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conducting polymer; polypyrrole; polythiophene; processing; solubility